

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b> A23D 9/00, A23L 1/30 B01J 13/02	<b>A1</b>	<b>(11) International Publication Number:</b> WO 94/01001 <b>(43) International Publication Date:</b> 20 January 1994 (20.01.94)
<b>(21) International Application Number:</b> PCT/DK93/00231 <b>(22) International Filing Date:</b> 6 July 1993 (06.07.93)  <b>(30) Priority data:</b> 0886/92                      6 July 1992 (06.07.92)                      DK  <b>(71) Applicant (for all designated States except US):</b> DANOCHE-MO A/S [DK/DK]; Malmparken 5, DK-2750 Ballerup (DK).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only) :</b> SKELBÆK, Tove [DK/DK]; Tingmosen 28, DK-3500 Værløse (DK). ANDERSEN, Steen [DK/DK]; Forhåbningsholms Allé 9B, 1.tv., DK-1904 Frederiksberg C (DK).  <b>(74) Agent:</b> LEHMANN & REE A/S; Grundtvigsvej 37, DK-1864 Frederiksberg C (DK).		<b>(81) Designated States:</b> AU, CA, JP, NZ, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> A MICROENCAPSULATED OIL OR FAT PRODUCT  <b>(57) Abstract</b>  The invention relates to a microencapsulated oil or fat product, wherein at least one oil or fat is dispersed in the matrix material as particles or drops having an average diameter of less than or equal to 2 µm, the oil or fat containing at least 10 % by weight of highly unsaturated fatty acid, preferably ω-3 and ω-6 fatty acids, the level of free fatty acids being below 5.0 % by weight and preferably below about 0.5 % by weight, and the matrix material consisting of caseinate and optionally at least one carbohydrate.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NE	Niger
BE	Belgium	GN	Guinea	NL	Netherlands
BF	Burkina Faso	GR	Greece	NO	Norway
BG	Bulgaria	HU	Hungary	NZ	New Zealand
BJ	Benin	IE	Ireland	PL	Poland
BR	Brazil	IT	Italy	PT	Portugal
BY	Belarus	JP	Japan	RO	Romania
CA	Canada	KP	Democratic People's Republic of Korea	RU	Russian Federation
CF	Central African Republic	KR	Republic of Korea	SD	Sudan
CG	Congo	KZ	Kazakhstan	SE	Sweden
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovak Republic
CM	Cameroon	LU	Luxembourg	SN	Senegal
CN	China	LV	Latvia	TD	Chad
CS	Czechoslovakia	MC	Monaco	TG	Togo
CZ	Czech Republic	MG	Madagascar	UA	Ukraine
DE	Germany	ML	Mali	US	United States of America
DK	Denmark	MN	Mongolia	UZ	Uzbekistan
ES	Spain			VN	Viet Nam
FI	Finland				

A microencapsulated oil or fat product.

5 The present invention relates to a microencapsulated oil or fat product containing at least one highly unsaturated fatty acid or a derivative thereof, a process of preparing the microcapsules and the use of the microencapsulated product in an infant formula and other functional foods.

10 Fat and oil products containing significant amounts of highly unsaturated fatty acids have recently been shown to possess valuable nutritional properties. Thus, US patent No. 4,670,285 describes an aqueous infant formula and an edible fat product for incorporation into an infant formula comprising highly unsaturated  $C_{20}$  or  $C_{22}$ ,  $\omega$ -6 fatty acids and  $C_{20}$  or  $C_{22}$ ,  $\omega$ -3 fatty acids which are considered to  
15 be of vital importance for the synthesis of structural lipids in the human brain. It also appears from said US 4 670 285 that infants and especially premature infants are unable to synthesize such unsaturated fatty acids in sufficient quantities.

20 EP-B1-231904 discloses a method for preparation of a fat mixture for infant feeds containing arachidonic and docosahexaenoic acid in a ratio of 2:1 to 3:1. According to the method various vegetable and animal fats or oils are heated, blended to obtain the desired fatty acid composition and stabilised by the addition of ascorbylic  
25 palmitate or alpha-tocopherol. The fat mixture can be used in the preparation of liquid or pulverized infant formulas.

30 Lipids containing unsaturated fatty acids, such as  $C_{20:4}$  and  $C_{22:4}$ ,  $\omega$ -6,  $C_{20:5}$ ,  $\omega$ -3 and  $C_{22:3}$ ,  $\omega$ -3, degrade easily under production of unpleasant tasting aldehydes (Pokorny, J. (1976) Effect of Non-lipidic Substances on Rancid Off Flavour of Lipids in Paoletti, R. et al. (eds.) Lipids, Vol. 2: Technology, p. 475-481, Raven Press, New York, 1976).

35 Thus, it is necessary to protect such lipids in e.g. food products from oxygen, trace metals and other substances which attack the double bonds of the highly unsaturated fatty acids in order to avoid off-flavour and loss of physiological activity and to increase the shelf life of products containing them. More specifically, there is

a need to provide microencapsulated fats or oils, such as vegetable and marine oils, wherein the highly unsaturated fatty acids are present in a digestible, shelf stable and undegradable form, preferably in a free flowing powdered form to be readily mixed with other dry or liquid components to form a nutritionally satisfying product, such as an infant formula, without the use of undesired additives.

GB-A-2,240,702 discloses a process for preparing fatty fodder additives with high content of  $\omega$ -3 fatty acids wherein a fat, e.g. fish oil, is heated to from 20 to 50°C with addition of an emulsifier such as monoglyceride or diglyceride to obtain an emulsion which is mixed with a carrier material such as casein and homogenized. The resulting emulsion is dried in a spray drier or in a fluid bed drier to obtain a powder.

JP patent publication No. 85-49097 discloses a powdered marine animal oil containing highly unsaturated fatty acids encapsulated in 3 to 40% of casein or caseinate, 3 to 60% of a saccharide, 1 to 5% of an emulsifier and 0 to 2% of microcrystalline cellulose.

US patent No. 5,013,569 discloses an infant food formulation and a powder or liquid concentrate for preparing an infant food formulation comprising the fatty acids DHA and EPA in a ratio of approximately 3:2, wherein the DHA and EPA may be protected from oxidation by exposure to ambient air by encapsulation. Suitable matrix materials are materials approved by the US Food and Drug Administration, i.e. compounds of the GRAS list, especially starches, cellulosic compounds and gums.

JP patent publication No. 90-305898 discloses powders of oils, such as fish oils, containing highly unsaturated fatty acids, obtained by spray drying an emulsion of said oils in a solution of a partial hydrolysate of casein at a hot air temperature of 140°C. The casein should be hydrolysed to a degree of from 5 to 20% in a protease catalyzed reaction in order to be a satisfying emulsifier. The powders obtained contain fatty oil in an amount of from 50 to 70%. It appears that sodium caseinate is an unsuitable emulsifier.

EP-A2-0 385 081 discloses the preparation of double encapsulated fat or oil emulsion products. The encapsulation method requires the film forming material, e.g. caseinate, to be added in two separate steps to an aqueous dispersion of an oil such as coconut oil, peanut oil  
5 or sunflower oil, to form an additional coating layer to obtain the desired oxidation resistance.

Singh, M. N.; Mathur, B.N. 1992. Indian J. Dairy Sci., 45, 5, p. 251-255, describe encapsulation of milk fat and vegetable oils in a  
10 matrix comprising whey proteins and mixtures of caseins and whey proteins. Due to the water insoluble nature of caseins, these proteins are used in various mixtures with the water soluble whey proteins in order to obtain a water dispersable dry product. It was  
15 concluded that encapsulation of fat globules with whey protein rather than casein improved the physical performance of the product.

None of the above citations discloses suitable powdered, protected lipid products, wherein the oil or fat contains at least 10% by weight of highly unsaturated fatty acid, preferably  $\omega$ -3 and  $\omega$ -6  
20 fatty acids, or a derivative thereof, which satisfy the requirements of the European Community to ingredients, such as encapsulation materials and emulsifiers, in infant formulas as published by the Commission of the European Community (EC) in a directive of May 14, 1991. US 5013569 suggests the use of gums and starches as wall  
25 material. However, gums, such as gum arabic, have been shown to inhibit mineral uptake in infants and the EC-allowed starches are unsuitable as matrix materials, because these starches cannot emulsify the fat or oil.

Caseinate is a water soluble proteinaceous film forming material which is a valuable nutrient, especially for infants. However, previous attempts to use caseinate as an encapsulation material for oil or fat has shown poor emulsifying properties (sodium caseinate, cf. JP 90-305898). Furthermore, EP-A2-0 385 081 shows the need for  
30 an additional coating layer when encapsulating oils and using caseinate as encapsulating material resulting in a less economic process.  
35

EP-A1-0,424,578 discloses a free flowing particulate composition

comprising from 70 to 95% of lipid e.g. fish oil containing from 10 to 50% of free fatty acids encapsulated in caseinate, preferably sodium caseinate. It appears from EP-A1-0 424 578 that the free fatty acid level must be above 10% by weight of the lipid in order to avoid leakage of lipid from a caseinate-protected product and it is considered important to homogenise an acidic lipid and an aqueous caseinate solution together at a temperature of at least 50°C. The emulsion is prepared by using a high-pressure ultrasonic homogeniser at a pressure of 14 to 16 bar. However, the free fatty acid level of natural animal and vegetable oils is normally below about 0.5-5.0% and the presence of free fatty acids in a food product is considered deleterious to the stability of the product.

The above citations do not disclose a microencapsulated oil or fat product, wherein at least one oil or fat is dispersed without the use of emulsifiers in the matrix material as particles or drops having an average diameter of less than or equal to 2  $\mu\text{m}$ , the oil or fat containing at least 10% by weight of highly unsaturated fatty acid, preferably  $\omega$ -3 and  $\omega$ -6 fatty acids, the level of free fatty acids being below 5.0% by weight and preferably below about 0.5% by weight, and the matrix material consisting of caseinate and optionally at least one carbohydrate.

It is therefore an object of the invention to provide a micro-encapsulated oil or fat product, wherein at least one oil or fat is dispersed in the matrix material as particles or drops having an average diameter of less than or equal to 2  $\mu\text{m}$ , the oil or fat containing at least 10% by weight of highly unsaturated fatty acid, preferably  $\omega$ -3 and  $\omega$ -6 fatty acids, the level of free fatty acids being below 5.0% by weight and preferably below about 0.5% by weight, and the matrix material consisting of caseinate and optionally at least one carbohydrate.

The microencapsulated oil or fat product of the invention can be used in foods, such as infant formulas, health functional foods, dietetic foods and pharmaceuticals, wherein a high content of a vegetable, animal or marine fat or oil containing at least one highly unsaturated fatty acid (HUFA) or a derivative thereof and wherein the content of free fatty acids is below 5% by weight, is

desired. The caseinate containing matrix material according to the invention is in itself a natural infant nutrient which does not contain any additives or the like and wherein the fat or oil is protected against degradation.

5

It is a further object to provide a microencapsulated vegetable, animal or marine fat or oil encapsulated in a caseinate based matrix material, wherein the ratio between AA and/or  $\gamma$ -linolenic acid, EPA and DHA is from 0.1:0.1:1 to 3:1:1 which corresponds to the ratio normally found in human milk.

10

The invention further provides a process of preparing a microencapsulated oil or fat product, wherein a mixture of an oil or fat having a content of at least 10% by weight of highly unsaturated fatty acid, preferably  $\omega$ -3 and  $\omega$ -6 fatty acids, or a derivative thereof and an aqueous solution of a caseinate and, optionally, carbohydrate containing matrix material is homogenised at a pressure of more than 200 bar, preferably more than 230 bar and more preferably more than 300 bar, and the resulting emulsion is dried using methods known per se to obtain free flowing microcapsules. The microcapsules thus prepared preferably contain fat or oil in an amount of from 10 to 65% by weight and free fatty acids in an amount of less than 5% by weight, preferably less than 0.5% by weight.

15

20

25

The use of caseinate as matrix material in the process according to the invention presents the following advantages:

30

35

- A free flowing microencapsulated product having a relatively high content of fat or oil and being nutritionally acceptable is obtained, because caseinate is in itself a protein nutrient which is preferred for feeding infants.
- It is possible in a one step emulsifying process to obtain a stable emulsion using caseinate as encapsulating material and as the only emulsifying agent and when the fat or oil to be emulsified comprises less than 5% by weight of free fatty acids, preferably less than 1% and more preferably less than 0.5% by weight of free fatty acid. Thus, the process of the invention makes it possible to prepare a stable emulsion using

a milk protein without the use of e.g. enzymes to first hydrolyse the protein or without the use of a fat or oil having an undesired high content of free fatty acids without the use of undesired additives, such as emulsifiers.

5

A preferred embodiment of the microencapsulated product of the invention has the following composition:

10 to 65, preferably 20 to 35 and more preferably 25% by weight of an oil or fat containing 0-75% of arachidonic acid ( $C_{20:4}$   $\omega$ -6, AA), 0-50% of eicosapentaenoic acid ( $C_{20:5}$   $\omega$ -3, EPA) and 0-100% of docosahexaenoic acid ( $C_{22:6}$   $\omega$ -3, DHA),

1 to 90, preferably 1 to 70 and more preferably 2 to 20% by weight of caseinate selected from the group consisting of sodium, potassium and calcium caseinate,

0 to 89, preferably 0 to 70, more preferably 20 to 70 and most preferably 30% by weight of a carbohydrate selected from the group consisting of glucose syrup, maltodextrin, saccharose, maltose or lactose.

0 to 10, preferably 5-6% by weight of at least one antioxidant selected from the group consisting of vitamin antioxidants, such as  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -tocopherols; ascorbic acid and derivatives thereof; carotenoids; and rosemary extract,

15 to 35, preferably 20 to 25% by weight of a spraying agent selected from the group consisting of corn starch; milk proteins, including casein, caseinate and whey proteins; preboiled or gelatinised starch; soy bean protein isolates; lactose; tricalcium phosphate; and calcium carbonate when a modified spray drying process is used. Spraying agent is not used in a normal spray drying process.

35

In a preferred embodiment of the process according to the invention 10-65%, preferably 20-35%, more preferably 25% by weight of the microencapsulated product of a fat or oil or a mixture of a fat or oil containing 0-75% of arachidonic acid ( $C_{20:4}$   $\omega$ -6, AA), 0-50% of



eicosapentaenoic acid ( $C_{20:5}$   $\omega$ -3, EPA) and 50-100%, preferably 0-100%, of docosahexaenoic acid ( $C_{22:6}$   $\omega$ -3, DHA), and an aqueous solution of from 1-98% caseinate, preferably 1-100%, more preferably 1-70%, and most preferably from 2-20% by weight of dry matter in solution, preferably sodium, potassium or calcium caseinate, most preferably potassium caseinate, is homogenised using a high-pressure homogenisator operated at 200 to at least 1000 bar, preferably from 230-300 to at least 1000 bar to obtain an emulsion wherein the oil drops have a diameter of from 0.01 to 5  $\mu$ m. Preferably more than 90% and more preferably more than about 95% of the oil drops have a diameter of from 0.01 to 2  $\mu$ m. The resulting emulsion is spray dried, preferably in a modified spray drying process at a hot air temperature of 70°C preferably under supply of a spraying agent, such as corn starch, powdered milk proteins, etc., to obtain a free flowing microencapsulated product having a particle diameter of from 10 to 600  $\mu$ m. When prepared in this manner the fat or oil is present in the emulsion or microcapsules in the form of drops having an average diameter of from 0.01 to 5  $\mu$ m, preferably more than 95% of the oil drops having a diameter of from 0.01 to 2  $\mu$ m more preferably from 0.01 to 1  $\mu$ m.

The emulsion may further contain 0-95%, preferably from 0 to 70% by weight and more preferably 20-70% of the dry product of a carbohydrate, preferably glucose syrup, maltodextrin, saccharose, maltose or lactose, most preferably maltodextrin or saccharose, and 0-15%, preferably 5 to 6% of the dry product of a vitamin antioxidant, preferably mix-tocopherol or ascorbic acid.

Although caseinate may be used as the only matrix material it is preferred to use a combination of caseinate and carbohydrate as matrix material. It has been found that a weight ratio between caseinate and carbohydrate of from 1:4 to 1:1 provides better mechanical stability to the microencapsulated product as well as a minimized proportion of free oil on the microcapsules.

The use of more than 65% by weight of fat or oil in the microencapsulated product and process according to the invention would result in a sticky product due to fat or oil residues on the surface of the microcapsules.

The term "highly unsaturated fatty acids" (HUFA) refers to nutritionally valuable fatty acids having at least 18 carbon atoms and having at least 3 double bonds. Preferred are  $\alpha$ -linolenic acid ( $C_{18:3}$   $\omega$ -3,  $\alpha$ -LNA),  $\gamma$ -linolenic acid ( $C_{18:3}$   $\omega$ -6,  $\gamma$ -LNA), arachidonic acid ( $C_{20:4}$   $\omega$ -6, AA), eicosapentaenoic acid ( $C_{20:5}$   $\omega$ -3, EPA), docosapentaenoic acid ( $C_{22:5}$   $n$ -3, DPA) and docosahexaenoic acid ( $C_{22:6}$   $\omega$ -3, DHA), more preferred are  $\gamma$ -LNA, AA, EPA and DHA, most preferred are AA, EPA and DHA. The fatty acids are normally present in natural oils as fatty acid esters of glycerol.

The fat or oil used in the microcapsules of the invention can be any fat or oil containing at least 10% by weight of HUFA, such as vegetable oil, e.g. evening primrose oil, borage oil, black currant seed oil, poppy seed oil; animal oil, e.g. egg yolk oil; single cell oil, e.g. alga oil; marine oil, e.g. fish oil. In the method according to the invention is preferably used mixtures of fat or oil, such as vegetable and fish oils to obtain a ratio between AA, EPA and DHA which equals the ratio in human milk. The fat or oil may be natural, fermented and/or enzymatically reesterified or chemically modified oil or fat.

Examples of additional matrix materials for use in the microcapsules according to the invention are preboiled or gelatinised starch.

Examples of antioxidants for use in the microcapsules of the invention are the vitamin antioxidants,  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -tocopherols, ascorbic acid and derivatives thereof, carotenoids, and rosemary extract. The antioxidants can be used in an amount of from 0 to 10% and preferably from 5 to 6% by weight of the final product. When hydrophilic antioxidants are used, such as ascorbic acid, these are preferably added to the solution of the matrix material and when lipophilic antioxidants are used, such as  $\alpha$ -tocopherol, these are preferably added together with the fat or oil.

Examples of spraying agents for use in the modified spray drying process are powders of corn starch, milk proteins, preboiled or gelatinised starch, soy bean protein isolates, lactose, tricalcium phosphate, and calcium carbonate.

5 The emulsion prepared according to the invention is stable for at least 1 hour and up to 1 week due to the small diameter of the oil drops and the use of caseinate as emulsifying agent. The emulsion can be dried using any conventional drying method, e.g. spray drying, modified spray drying, fluid bed drying or drum drying. Modified spray drying is preferred because lower process temperatures can be used and more spherical and dense particles can be obtained. Modified spray drying is preferably effected at an air temperature of between 40°C and 140°C, more preferably between 60°C and 100°C. As a spraying agent is preferably used corn starch, or milk protein powder, preferably casein powder, in an amount which corresponds to from 15 to 35% by weight, preferably from 20 to 25% by weight of the dry product. Conventional spray drying is preferably effected at a temperature of from 140 to 300°C.

15 The invention further relates to the use of a microencapsulated oil or fat product containing at least 10% by weight of highly unsaturated fatty acids, preferably  $\omega$ -3 and  $\omega$ -6 fatty acids, or derivatives thereof dispersed in a matrix material comprising caseinate, preferably sodium, potassium and calcium caseinate, most preferably potassium caseinate, in dry or wet mixture with an infant formula, a health functional food, a dietetic food, a nutrient for diabetics, a protein cure for weakened patients, or a pharmaceutical.

25 The ratio in the oil or fat based on weights of AA and/or  $\gamma$ -linolenic acid, EPA and DHA is between 0:0:1 and 3:1:1, preferably about 0.1:0.1:1 and more preferably about 0.5:0.12:0.3, which is commonly found in human milk.

30 The oils used in the microencapsulated product of the invention are preferably fish oils having a high percentage of highly unsaturated fatty acids, preferably more than about 30% by weight, or borage oil having more than about 20% by weight of highly unsaturated fatty acids. Said oils are very susceptible to oxidation and also in comparison to vegetable oils, such as sunflower oil, having a high proportion of unsaturated fatty acids. The following test shows the duration of the induction period before oxidation takes place in a sample of various oils used in the product of the invention compared

to typical vegetable oils used in infant formulas:

Oxidation test for oils

5	Apparatus:	Rancimat 617, Metrohm, Switzerland	
	Test conditions:	100°C/20l air per hour	
	Results:	Oil	Duration
10		15:15(EPA:DHA) fish oil	51 min
		5:25(EPA:DHA) fish oil	54 min
		18:12(EPA:DHA) fish oil	0 min
		Coconut oil	>100 hours
		Sunflower oil	6 hours
15		Peanut oil	11 hours

20 The oxidation test shows that highly unsaturated oils, such as fish oils, are extremely susceptible to oxidation. Nevertheless, the microencapsulated product of the invention containing these susceptible oils are stable for at least one year as will appear from the following examples.

Example 1

25 Potassium caseinate (40 g) was dissolved in water (380 g) having a temperature of 60°C. Maltodextrin DE 24-30 (80 g) was added and dissolved. The solution was de-oxygenised under vacuum and sodium ascorbate (16,2 g) was added. (90 g) of fish oil having a content and ratio of AA, EPA and DHA of 4%: 6%:23% was emulsified into the  
30 solution using a Rannie high-pressure homogenisator (Model MINI-LAB, type 8.30 H) at 800 bar to obtain oil drops in the emulsion whereof 95% have a diameter of from 0.01 to 2 µm.

35 This emulsion was stable for at least 2 days.

Example 2

Example 1 was repeated using potassium caseinate (400 g), water (2933 g), maltodextrin DE 24-30 (1600 g), sodium ascorbate (249 g)

and fish oil (1100 g) having a content and ratio of EPA and DHA of 15%:15%. The emulsion temperature was 68°C.

5 The emulsion was dried using a modified spray drying process at 80°C under the supply of casein powder which constituted 20% of the dried product. The resulting product containing 25% fat or oil and 4% residual moisture has a particle size of from 10 to 600  $\mu\text{m}$  and is stable for 2 years.

10 The fatty acid composition of a typical fish oil having a ratio of EPA and DHA of 15%:15% is as follows:

	<u>Fatty acids</u>	<u>%</u>	<u>% of total fat</u>
15	<u><math>\omega</math>-n</u>		38.6%
	18:3	0.7	
	18:4	2.9	
	20:4	1.2	
20	20:5	14.6	
	21:5	0.6	
	22:5	2.6	
	22:6	16.0	
25	<u>Polyunsaturates other than <math>\omega</math>-3</u>		11.6%
	16:3	1.1	
	18:2	1.2	
	20:4 $\omega$ -6	0.9	
30	others	8.4	
	<u>Monounsaturates</u>		19.0%
	16:1	8.2	
35	18:1	7.8	
	others	3.0	
	<u>Saturates</u>		30.8%

14:0	6.7
16:0	18.3
others	5.8

5

Example 3

Potassium caseinate (170 g) was dissolved in 1240 g of water at a temperature of 60°C.

10

Sodium ascorbate (30,6 g) was added and 170 g of fish oil was emulsified into the solution using a Rannie high-pressure homogenisator 3 times at 400 bar, 600 bar and 800 bar to obtain an average oil drop diameter of below 0.7  $\mu\text{m}$ . The emulsion was dried as in Example 2 using an emulsion temperature of 60°C.

15

Example 4

The effect of emulsifying at varying pressure using a high-pressure Rannie homogenisator (Model MINI-LAB, type 8.30 H) was tested and the results are given below:

20

The following ingredients were used as in Example 2:

25

Water	2933 g
Potassium caseinate	400 g
Maltodextrin	1600 g
Sodium ascorbate	249 g
Fish oil, 15%:15% of EPA:DHA	1100 g

30

The emulsion was passed through the homogenisator 3 times.

35

Table

	Applied pressure, bar	Average oil drop diameter, $\mu\text{m}$	Maximum oil drop diameter, $\mu\text{m}$	Stability of emulsion at 60°C h
5	50	4	20	0.5 h
	100	3	10	1 h
10	200	1-2	10	at least 3 days
	230	<0.7	4.0	-
	270	<0.7	4.0	-
	300	<0.7	4.0	at least 3 days
	400	<0.7	4.0	at least 3 days
15	600	<0.7	3.0	at least 3 days

20 The average oil drop diameter was measured after 1 and 24 hours for  
 emulsions prepared at 200, 300, 400 and 600 bar and no changes were  
 observed. The effect of emulsifying at pressures above about 200 bar  
 is that a stable emulsion is obtained through a small oil drop  
 diameter, said diameter being stable for several hours. The oil drop  
 diameter decreases with the use of increasing pressures and it can  
 be expected that an upper limit of applied pressure only depends on  
 the available equipment. The emulsion prepared at 50 bar was not  
 25 satisfying due to separation after only 1/2 hour.

30

35

C l a i m s

1. A microencapsulated oil or fat product, wherein at least one oil or fat is dispersed in the matrix material as particles or drops having an average diameter of less than or equal to 2  $\mu\text{m}$ , the oil or fat containing at least 10% by weight of highly unsaturated fatty acid, preferably  $\omega$ -3 and  $\omega$ -6 fatty acids, the level of free fatty acids being below 5.0% by weight and preferably below about 0.5% by weight, and the matrix material consisting of caseinate and optionally at least one carbohydrate.
2. Microencapsulated product according to claim 1, wherein the oil or fat is a marine oil, preferably a fish oil, containing at least 30% by weight of  $\omega$ -3 fatty acids.
3. Microencapsulated product according to claim 1, wherein the oil or fat is a vegetable oil, preferably borage oil, containing at least 20% by weight of  $\omega$ -3 and/or  $\omega$ -6 fatty acids.
4. Microencapsulated product according to any one of the preceding claims, wherein the oil or fat is a natural, fermented and/or enzymatically reesterified or chemically modified oil or fat, preferably in an amount of from 10 to 65% by weight; the matrix material comprises from 1 to 100% by weight caseinate and from 0 to 70% by weight of at least one carbohydrate selected from the group consisting of glucose syrup, maltodextrin, saccharose, maltose or lactose; from 0 to 10% by weight of at least one antioxidant selected from the group consisting of the vitamin antioxidants  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -tocopherols, ascorbic acid and derivatives thereof, carotenoids, and rosemary extract, and from 0 to 35% by weight of a spraying agent selected from the group consisting of corn starch, milk proteins, including casein, caseinate and whey proteins, preboiled or gelatinised starch, soy bean protein isolates, lactose, tricalcium phosphate, and calcium carbonate.
5. Microencapsulated product according to any one of the preceding claims, which comprises from 20 to 35% by weight fat or oil, preferably 25% by weight oil or fat, from 2 to 20% by weight caseinate, preferably 15% by weight caseinate, and from 20 to 70% by



weight carbohydrate, preferably 30% by weight carbohydrate, from 5 to 6 % by weight antioxidant, and from 20 to 25% of a spraying agent.

5 6. Microencapsulated product according to any one of the preceding claims, wherein the oil is a fish oil, the caseinate is sodium, potassium, or calcium caseinate, preferably potassium caseinate, and the carbohydrate is maltodextrin or saccharose, and the antioxidant is selected from the group consisting of  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  tocopherols, 10 ascorbic acid and derivatives thereof, and carotenoids.

7. Microencapsulated product according to any one of the preceding claims, wherein the matrix material comprises a caseinate and carbohydrate in a weight ratio of from 1:4 to 1:1. 15

8. Use of a microencapsulated oil or fat product wherein the oil or fat containing at least 10% by weight of highly unsaturated fatty acids, preferably  $\omega$ -3 and  $\omega$ -6 fatty acids, is dispersed in a matrix material comprising caseinate in dry or wet mixture with an infant formula. 20

9. Use of a microencapsulated oil or fat product wherein the oil or fat containing at least 10% by weight of highly unsaturated fatty acids, preferably  $\omega$ -3 and  $\omega$ -6 fatty acids, is dispersed in a matrix material comprising caseinate in dry or wet mixture with a health functional food, a dietetic food, a nutrient for diabetics, a protein cure for weakened patients, or a pharmaceutical. 25

10. Use of the microencapsulated product according to any one of claims 1 to 7 dry or wet mixed with an infant formula. 30

11. Use of the microencapsulated product according to claim 10, wherein the oil or fat contains less than 20% by weight and preferably less than 15% by weight of EPA and more than 15% by weight and preferably more than 20% by weight of DHA. 35

12. Use of the microencapsulated product according to claim 10, wherein the ratio of AA and/or  $\gamma$ -linolenic acid, EPA, and DHA in the oil or fat is from 0.1:0.1:1 to 3:1:1.

13. Use of the microencapsulated product according to any one of  
claims 1 to 7 dry or wet mixed with a health functional food, a  
dietetic food, a nutrient for diabetics, a protein cure for weakened  
5 patients, or a pharmaceutical.

14. A process of preparing the microencapsulated product according  
to any one of the preceding claims, wherein a mixture of an oil or  
fat having a content of at least 10% highly unsaturated fatty acid,  
10 preferably  $\omega$ -3 and  $\omega$ -6 fatty acids, and an aqueous solution of a  
caseinate and, optionally, carbohydrate containing matrix material  
is homogenised at a pressure of more than 200 bar and the resulting  
emulsion is dried using methods known per se to obtain free flowing  
microcapsules.  
15

15. Process according to claim 14, wherein the mixture is homogen-  
ised at a pressure of at least 230 bar, preferably at least 300 bar.

20

25

30

35

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/DK 93/00231

## A. CLASSIFICATION OF SUBJECT MATTER

IPC5: A23D 9/00, A23L 1/30, B01J 13/02

According to International Patent Classification (IPC) or to both national classification and IPC

## R. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: A23D, A23L, B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, USPM

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB, A, 2217173 (B A WHITTLE), 25 October 1989 (25.10.89), claims 1-4,9-12 --	1-15
A	EP, A2, 0425213 (UNILEVER PLC ET AL.), 2 May 1991 (02.05.91), claims 1-24 --	1-15
A	Indian J. Dairy Sci., Volume 45, No 5, 1992, M.N. Singh et al., "RECONSTITUTION BEHAVIOR OF SPRAY-DRIED INFANT FORMULA AS AFFECTED BY THE TYPE OF MILK PROTEINS EMPLOYED FOR ENCAPSULATION OF FAT" page 251 - page 255 ---	1-15

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*R\* document referring to an oral disclosure, use, exhibition or other means
- \*T\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

\*&amp;\* document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

14 Sept 1993

20-09-1993

Name and mailing address of the ISA/  
Swedish Patent Office  
Box 5055, S-102 42 STOCKHOLM  
Facsimile No. +46 8 666 02 86

Authorized officer

INGA-KARIN PETERSSON  
Telephone No. +46 8 782 25 00

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/DK 93/00231

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 5106639 (LEE N-H ET AL.), 21 April 1992 (21.04.92), claims 1-2,5,11-14  --	1-15
A	US, A, 3968261 (GOODMAN L.P.), 6 July 1976 (06.07.76), column 2, line 26 - column 4, line 20; column 4, line 53 - column 5, line 67  -- -----	1-15

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

26/08/93

International application No.  
PCT/DK 93/00231

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
GB-A-	2217173	25/10/89	NONE		
EP-A2-	0425213	02/05/91	NONE		
US-A-	5106639	21/04/92	GB-A-	2240702	14/08/91
US-A-	3968261	06/07/76	CA-A-	1064319	16/10/79

